

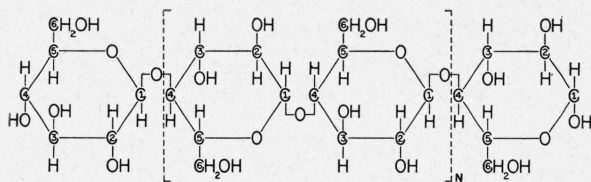
Spectrophotometric Determination of Carboxyl in Cellulose¹

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A method that uses the intensity of the absorption of the oxidized celluloses at 5.8 microns as a measure of their carboxyl content is described. The analyses are carried out on mineral oil slurries of 1:1 mixtures of finely divided polystyrene and cellulose. The absorption of the polystyrene at 6.2 microns is used as a reference band, thus obviating the necessity of accurately controlling the thickness of the absorption cell. The method gives results that agree fairly well with those obtained by the calcium acetate method and can be used to detect as little as 0.1 millimole of carboxyl per gram of cellulose.

I. Introduction

Cellulose products are frequently exposed to oxidative environments during manufacture and use. The oxidation of cellulose, commonly represented by the formula below is, therefore, of great technical importance.



The types of oxidation theoretically possible for cellulose are:

Oxidation of primary alcohol groups (carbon 6 of the anhydroglucose units) to aldehyde or carboxyl groups.

Oxidation of secondary alcohol groups (carbon 2 or 3) to ketone groups.

Oxidation of glycol groups (carbons 2 and 3) to aldehyde or carboxyl groups with attendant cleavage of the carbon-to-carbon bond.

Oxidation of hemiacetal groups (carbon 1) to carboxyl groups. Although this type of oxidation is unimportant in undegraded celluloses where the number of terminal groups is extremely small, it may be of importance in certain degraded celluloses.

With few exceptions [1 to 5],² oxidants appear to be nonselective in their action on cellulose, giving rise to two or more of the above types of oxidation simultaneously. Accordingly, for the characterization of oxidized celluloses, methods capable of detecting, estimating, and allocating ketone, aldehyde, and carboxyl groups in the presence of each other are needed. Available chemical methods are not entirely satisfactory for this purpose.

The presence of carbon attached to oxygen by means of a double bond in the aforementioned groups suggests that oxidized celluloses will show the char-

acteristic absorption of the C=O stretching vibrations in the 5.5- to 6.5- μ region of the spectrum. As the frequency and intensity of this absorption are normally influenced by the adjacent molecular structure [6, 7], ketonic, aldehydic, and carboxylic carbonyl groups of oxidized celluloses might reasonably be expected to absorb at different wavelengths. If such is the case, infrared spectrophotometry should be useful in the analysis and characterization of oxidized celluloses.

During earlier work in this laboratory, an absorption band at 5.8 μ was observed in the spectra of films of regenerated cellulose that had been subjected to moderate oxidation with nitrogen dioxide [8, 9]. Under the conditions used, this reagent is selective in its action on cellulose, resulting only in the conversion of primary alcohol groups to carboxyl groups [1, 2]. The absorption of these films at 5.8 μ was, consequently, attributed to carboxylic carbonyl. Subsequent examination of spectra of mineral oil slurries of cottons that had been treated with a variety of oxidants showed absorption at 5.8 μ to be of frequent occurrence. Although it was recognized that noncarboxylic carbonyl might be responsible for this absorption in some cases, the possibility of using the intensity of the absorption of the oxidized celluloses at 5.8 μ as a measure of their carboxyl content was investigated. The results of this investigation are presented in this report.

The use of the intensity of an absorption band as a measure of the concentration of the group or compound responsible for the band is based on Beer's law. This law states that $\log I_0/I = kcd$, where I_0 and I are the intensities, respectively, of the radiant energy of a given wavelength falling upon and passing through the sample, k is an absorption coefficient characteristic of the sample, c is a concentration, and d is the cell thickness. In the analysis of discontinuous solids, such as the oxidized celluloses, the necessity for measuring cell thickness is usually avoided by the addition of a properly chosen solid reference material in a fixed ratio to the total sample [7, 10]. Spectrophotometric measurements on mixtures of the reference material with samples containing varying and known amounts of the component of interest supply the data required

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² Figures in brackets indicate the literature references at the end of this paper.

for the construction of a working curve to be used in the analysis of unknowns. The curve is obtained by plotting the concentration of the component of interest against the ratio of $\log I_0/I$ for the wavelength of interest in the sample to $\log I_0/I$ for a wavelength at which the reference material absorbs.

II. Construction of an Analytical Working Curve

In the present work, data for the construction of an analytical working curve were obtained from spectra of mineral oil slurries of 1:1 mixtures of cellulose samples of known carboxyl content with finely divided polystyrene, which provided a reference absorption band at 6.2μ . The polystyrene was obtained from the manufacturer, the Dow Chemical Co., in granular form. Prior to use, it was ground to a fine powder in a vibratory ball mill [11], washed with 95 percent ethanol and dried in air.

Empire cotton purified by a modification of the procedure described by Worner and Mease [12] and milled for 30 min in the vibratory ball mill, was used as a diluent in the preparation of cellulose samples of known carboxyl content. A nitrogen-dioxide-oxidized cotton prepared by the Tennessee Eastman Corp. was used as the source of carboxyl. This oxidized cellulose had been ground in a Wiley mill to pass a 100-mesh screen, freed of water-soluble material by repeated extraction with water, and dehydrated by successive treatments with absolute methanol and benzene. The benzene was removed by prolonged storage over paraffin in vacuum.

Before use, the cotton, oxidized cotton, and polystyrene were conditioned at 65-percent relative humidity at 21°C . The carboxyl contents of the conditioned cotton and nitrogen-dioxide-oxidized cotton as determined by the calcium acetate method [1] were 0.01 and 1.78 millimoles per gram. This sample of nitrogen-dioxide-oxidized cotton was used in preference to a more highly oxidized sample in order to keep the concentration of noncarboxylic carbonyl to a minimum [1,13]. The quantities of cotton and oxidized cotton used were such that the total weight of each cellulose sample was 100 mg.

The cellulose samples were dry-mixed with an equal weight of polystyrene and were then milled with 0.5 ml of mineral oil between weighted ground glass plates. For the absorption measurements, the resulting slurries were injected into demountable rock-salt absorption cells equipped with silver or cellulose acetate spacers of approximately 25, 50, or 100μ in thickness. The spacers were chosen in such a way that the values for the transmission at 5.8μ ranged from 30 to 60 percent.

Spectra were obtained with a double-beam automatic recording Baird spectrophotometer [14] equipped with a sodium chloride prism. The performance of the instrument was checked frequently against a polystyrene film of known spectral characteristics. The single-cell rather than the double-cell method was used in securing spectra. In order to compensate for variations in the behavior of the

spectrophotometer, four to six spectra were recorded for each absorption cell. Values for I_0 at 5.8 and 6.2μ could not be obtained directly from the spectrograms. They were, therefore, assumed to be equal to the percentage transmission at nearby wavelengths at which neither oxidized cellulose nor polystyrene has absorption bands—namely, 5.5 and 6.4μ . Average values for the ratio,

$$\frac{\log (I_0/I)_{5.8\mu}}{\log (I_0/I)_{6.2\mu}},$$

were used in the construction of the working curve and in spectrophotometric analyses.

In figure 1 are shown the 5.2- to 6.5μ region of the spectra of mineral oil slurries of three of the polystyrene-cellulose mixtures. For comparison, spectra of mineral oil slurries of the polystyrene, cotton, and nitrogen-dioxide-oxidized cotton are given in figure 2. In table 1, the values of the ratio,

$$\frac{\log (I_0/I)_{5.8\mu}}{\log (I_0/I)_{6.2\mu}},$$

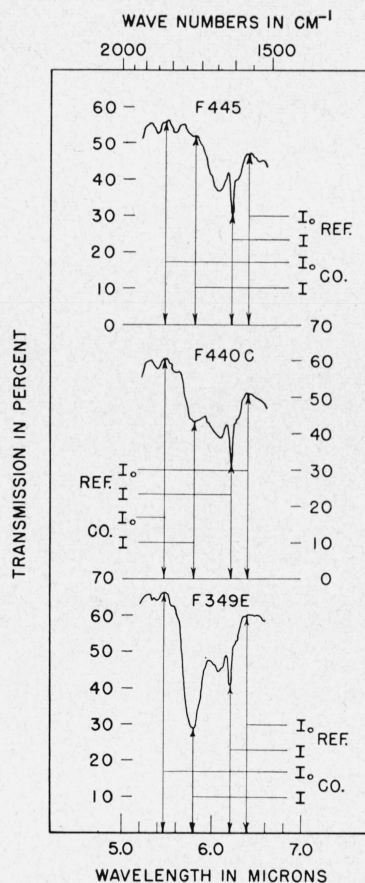


FIGURE 1. Spectrograms of mineral oil slurries of 1:1 mixtures of polystyrene with cellulose samples of known carboxyl content showing method of obtaining values of I_0 and I for carboxylic carbonyl and reference bands.

F445, 0.01 millimoles COOH/g cellulose; F440C, 0.54 millimoles COOH/g cellulose; F349E, 1.78 millimoles COOH/g cellulose.

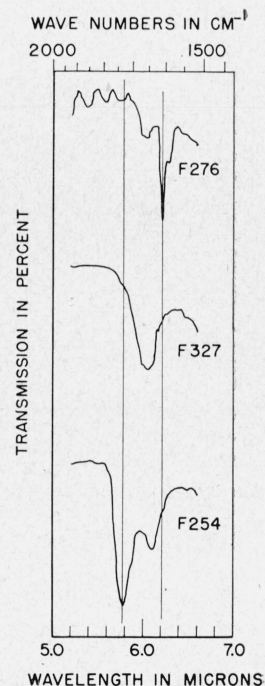


FIGURE 2. Spectrograms of mineral oil slurries of F276, polystyrene; F327, cotton; F254, nitrogen-dioxide-oxidized cotton.

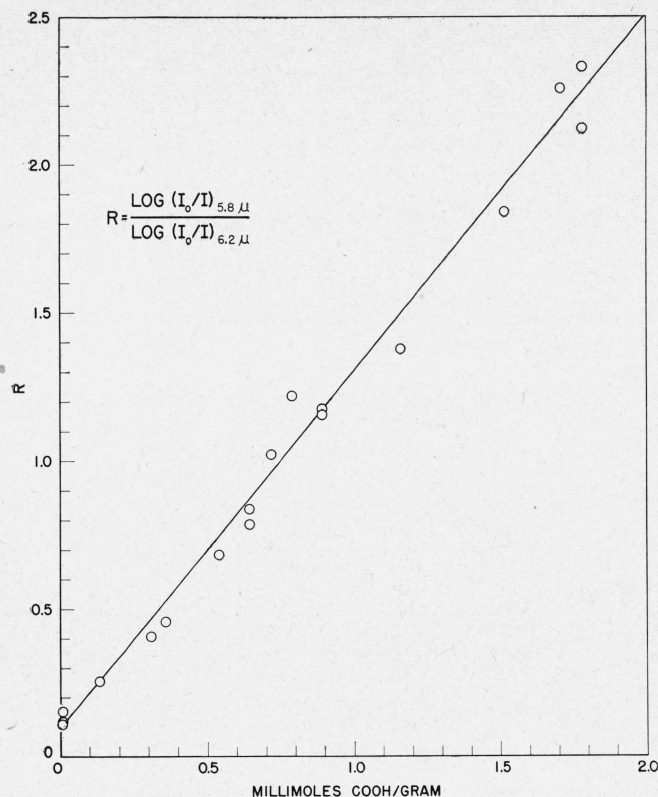


FIGURE 3. Analytical working curve for determination of carboxyl in cellulose.

are given with the carboxyl contents of the cellulose samples. A comparison of the plot of these data with the straight line obtained by the application of the method of least squares to the experimental data, both presented in figure 3, shows that

$$\frac{\log (I_0/I)_{5.8\mu}}{\log (I_0/I)_{6.2\mu}}$$

is essentially a linear function of the concentration of carboxyl in the cellulose samples. The actual values of the points plotted have an uncertainty of about one-twentieth of a unit.

The failure of the straight-line plot to pass through the origin as required by Beer's law is the result of

TABLE 1. Spectrophotometric measurements on 1:1 mixtures of polystyrene with cellulose of known carboxyl content

Carboxyl content of cellulose	$\frac{\log (I_0/I)_{5.8 \mu}}{\log (I_0/I)_{6.2 \mu}}$	Carboxyl content of cellulose	$\frac{\log (I_0/I)_{5.8 \mu}}{\log (I_0/I)_{6.2 \mu}}$
<i>Millimoles/g</i>		<i>Millimoles/g</i>	
0.01	0.15	0.79	1.22
.01	.12	.89	1.32
.01	.11	.89	1.18
.13	.26	.89	1.15
.31	.41	1.16	1.38
.36	.46	1.52	1.84
.54	.68	1.71	2.26
.64	.79	1.78	2.33
.64	.84	1.78	2.12
.72	1.02		

the arbitrary procedure employed in obtaining values for I_0 from the spectrograms. It should not affect the usefulness of the plot as an analytical working curve.

III. Analysis of Oxidized Celluloses

As a check on the general utility of the analytical working curve, it was used in the analysis of 11 oxidized celluloses. Using the procedure outlined above, values for the ratio,

$$\frac{\log (I_0/I)_{5.8\mu}}{\log (I_0/I)_{6.2\mu}}$$

were obtained for 1:1 mixtures of polystyrene with the oxidized celluloses. The concentrations of carboxyl in the oxidized celluloses were then read directly from the working curve.

The oxidants used in the preparation of the oxidized celluloses were air at 145° C, chromic oxide in a mixture of glacial acetic acid and acetic anhydride [15], hydrogen peroxide [16, p. 114], potassium dichromate in oxalic acid solution [16, p. 114], potassium permanganate in sulfuric acid solution [16, p. 112], bromine in the presence of excess barium carbonate [17], buffered periodic acid [18, 19], and nitrogen dioxide [1]. With the exception of the two nitrogen-dioxide-oxidized cottons and one of the periodate-oxidized cottons that were prepared, respectively, by the Tennessee Eastman Corp. and R. E. Reeves of the Southern Regional Research Laboratory, all of the oxidized cottons were prepared from purified Empire cotton that had been ground in a Wiley mill to pass a 20-mesh screen. The fact that the cotton was added to the oxidant without previous swelling probably accounts for the low degree of oxidation observed in most samples.

The results of the spectrophotometric analyses are given in table 2. Also given are the values obtained for carboxyl and noncarboxylic carbonyl by the calcium acetate [1] and hydroxylamine hydrochloride [15] methods. In table 3 are given the results of 13 analyses for carboxyl carried out on a single oxidized cotton over a 3-month period by 2 different analysts as a check on the precision of the spectrophotometric method. The values obtained for carboxyl by the spectrophotometric and calcium acetate methods agree fairly well. The greatest difference observed, 0.34 millimoles per gram for a nitrogen-dioxide-oxidized cotton, is of doubtful significance, as the yellow color of this oxidized cotton introduced considerable uncertainty in the determination of carboxyl by the calcium acetate method. Difficulty was also encountered in applying the calcium acetate method to the periodate-oxidized cottons. Thus, here also the value obtained by the spectrophotometric method may be the more reliable of the two. In general, the results indicate that the intensity of the absorption of the oxidized celluloses at 5.8 μ constitutes a fairly satisfactory measure of their carboxyl content even in the presence of appreciable amounts of non-carboxylic

carbonyl. When measured according to the procedure described in this report, as little as 0.1 millimole of carboxyl per gram of cellulose can be detected.

TABLE 2. *Analyses of oxidized celluloses*

Oxidant used in preparation of oxidized cellulose	Carboxyl by calcium acetate method	Carboxyl by spectrophotometric method	Deviation	Noncarboxylic carbonyl by hydroxylamine hydrochloride method
	Millimole/g 0.02	Millimole/g 0.04	Millimole/g +0.02	Millimole/g 0.40
Air at 145° C.....				
CrO ₃ /acetic acid-acetic anhydride.....	.00	.02	+ .02	.95
H ₂ O ₂04	.06	+ .02	.98
K ₂ Cr ₂ O ₇ /oxalic acid.....	.04	.02	- .02	.44
KMnO ₄ /H ₂ SO ₄44	.56	+ .12	.18
Br ₂ /BaCO ₃38	.40	+ .02	1.19
Br ₂ /BaCO ₃66	.68	+ .02	0.38
HIO ₄02	.19	+ .17	7.37
HIO ₄09	.19	+ .10	-----
NO ₂	1.40	1.39	- .01	-----
NO ₂	2.65	2.31	- .34	-----

TABLE 3. *Spectrophotometric analyses of potassium-permanganate-oxidized cotton*

Sample	Carboxyl	Deviation from mean
	Millimole/g	Millimole/g
1.....	0.46	-0.10
2.....	.59	+ .03
3.....	.56	.00
4.....	.61	+ .05
5.....	.55	- .01
6.....	.61	+ .05
7.....	.52	- .04
8.....	.53	- .03
9.....	.53	- .03
10.....	.58	+ .02
11.....	.53	- .03
12.....	.66	+ .10
13.....	.59	+ .03
	0.56 mean	±0.04 average deviation from mean

IV. Summary

Details of a spectrophotometric method for the quantitative estimation of carboxyl in cellulose are

given. The method gives results that are in fair agreement with those obtained by the calcium acetate method and can be used to detect as little as 0.1 millimole of carboxyl per gram.

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V. REFERENCES

- [1] E. C. Yackel and W. O. Kenyon, *J. Am. Chem. Soc.* **64**, 121 (1942).
- [2] C. C. Unruh and W. O. Kenyon, *J. Am. Chem. Soc.* **64**, 127 (1942).
- [3] H. A. Rutherford, F. W. Minor, A. R. Martin, and M. Harris, *J. Research NBS* **29**, 131 (1942) RP1491.
- [4] E. L. Jackson and C. S. Hudson, *J. Am. Chem. Soc.* **60**, 989 (1938).
- [5] G. F. Davidson, *Shirley Inst. Memoirs* **18**, 69 (1941).
- [6] H. M. Randall, R. G. Fowler, N. Fuson, and J. R. Dangle, *Infrared determination of organic structures* (D. Van Nostrand Co., Inc., New York, N. Y., 1949).
- [7] R. B. Barnes, R. C. Gore, U. Liddel, and Van Z. Williams, *Infrared spectroscopy* (Reinhold Publishing Co., New York, N. Y., 1944).
- [8] J. W. Rowen, C. M. Hunt, and E. K. Plyler, *J. Research NBS* **39**, 133 (1947) RP1816.
- [9] J. W. Rowen and E. K. Plyler, *J. Research NBS* **44**, 313 (1950) RP2080.
- [10] R. B. Barnes, R. C. Gore, E. F. Williams, S. G. Linsley, and E. M. Petersen, *Anal. Chem.* **19**, 620 (1947).
- [11] F. H. Forziati, W. K. Stone, J. W. Rowen, and W. D. Appel, *J. Research NBS* **45**, 109 (1950) RP 2116.
- [12] R. K. Worner and R. T. Mease, *J. Research NBS* **21**, 609 (1938) RP1146.
- [13] P. A. McGee, W. F. Fowler, Jr., C. C. Unruh, and W. O. Kenyon, *J. Am. Chem. Soc.* **70**, 2700 (1948).
- [14] W. S. Baird, H. M. O'Bryan, G. Ogden, and D. Lee, *J. Opt. Soc. Am.* **37**, 754 (1947).
- [15] E. K. Gladding and C. B. Purves, *Paper Trade J.* **116**, 150 (1943).
- [16] C. Doree, *The methods of cellulose chemistry*, 2d ed. (D. Van Nostrand Co., Inc., New York, N. Y., 1947).
- [17] O. Faber and B. Tollens, *Ber. deut. chem. Ges.* **32**, 2592 (1899).
- [18] D. H. Grangaard, E. K. Gladding, and C. B. Purves, *Paper Trade J.* **115**, 75 (1942).
- [19] R. Adams, Editor, *Organic reactions*, vol. II (John Wiley & Sons, New York, N. Y., 1944).

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